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MOLECULAR DYNAMICS OF CHEMICAL REACTIONS IN SOLUTION

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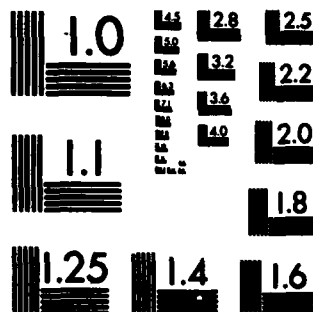
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REACTIONS IN SOLUTION

by

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## MOLECULAR DYNAMICS OF CHEMICAL REACTIONS IN SOLUTION

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### ABSTRACT

↙ We hope to answer one of the most fundamental and important unsolved questions in chemistry: how, from a molecular perspective, do chemical reactions in solution actually occur. The key to solving this long-standing problem is to understand the molecular dynamics, i.e. the motions of the atoms and the forces that drive them. We have already developed theoretical techniques and computational procedures involving specialized computer hardware needed to calculate the molecular dynamics for many chemical reactions in solution. From the dynamics we have derived the interface for experimental verification, namely transient electronic, infrared, and Raman spectra as well as x-ray diffraction, all of which are potentially observable manifestations of the atomic motions during the reaction. We have tested our approach on the simple inorganic  $I_2$  photodissociation and solvent caging reaction. The agreement between molecular dynamics based theory and experimental picosecond transient electronic absorption spectrum as a function of solvent, time, and wavelength is sufficiently close as to indicate that for the first time we are discovering at least part of the molecular dynamics by which a real solution chemical reaction takes place.

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# **MOLECULAR DYNAMICS OF CHEMICAL REACTIONS IN SOLUTION**

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## **I. INTRODUCTION**

The vast majority of the reactions of interest to chemists occur in solution, including most of inorganic, organic, industrial, and bio-chemistry. It is thus ironic that there is not yet a single solution chemical reaction which is understood from the microscopic point of view of the atomic motions, i.e. the molecular dynamics, by which it occurs. Therefore, one of the fundamental and important questions of chemistry remains unsolved. Answering this question is important not just from the viewpoint of pure research, but also because an understanding of how solution reactions actually occur can be expected to lead to an increased ability to control such reactions for useful ends.

We believe that there is a general approach which can lead to the discovery of the molecular dynamics for a wide variety of inorganic, organic, and biochemical solution reactions. Such a general approach requires both theory and experiment, as only theory can provide a complete view of the molecular dynamics and only experiment can sufficiently test the theoretical predictions that we should have confidence in them. Our approach has three parts. First, we have developed the computational techniques to calculate the molecular dynamics for reactant-solvent systems involving hundreds to thousands of atoms. This has been accomplished by the use of specialized computer hardware, an array processor,<sup>1,2</sup> allowing us to run approximately 35 times faster than on the DEC VAX 780 we also use. Second, we need an interface between theory and experiment, a set of phenomena which closely reflect the atomic motions by which reactions occur and which equally can be computed theoretically and measured experimentally. Our choice for this interface is transient spectra. Therefore we have developed the theoretical and computational techniques to calculate infrared,<sup>3,4</sup> Raman,<sup>4,6</sup> and electronic<sup>7,8</sup> spectra, as well as x-ray diffraction<sup>9</sup> from molecular dynamics. Third, we have begun to experimentally measure transient spectra from chemical reactions on the picosecond time scale. We present below transient electronic absorption from a chemical reaction,<sup>6,8</sup> as both theoretically computed from molecular dynamics and experimentally measured.

We have demonstrated this approach for the chemical reaction of  $I_2$  photodissociation in various solvents, followed by solvent caging, atomic recombination, and the decay of the excess energy in the newly formed vibrationally hot  $I_2$  back to the solvent. We have computed the molecular dynamics for this reaction sequence in several solvents, and from the dynamics computed the time dependent electronic absorption<sup>7,8,10</sup> and Raman spectra<sup>4,6</sup> as well as the transient x-ray diffraction.<sup>9</sup> To check the dynamics, we have constructed a picosecond transient electronic spectrometer<sup>11,12</sup> and measured the transient electronic absorption for this reaction in a variety of

solvents.<sup>7,8</sup> The agreement between theory and experiment as a function of nature of solvent, of time scale, and of probe photon energy is most gratifying, giving us some reason to hope that for the first time we are actually discovering at least part of the molecular dynamics by which a real reaction in solution takes place. A hypothesis to explain the wide variation in molecular dynamic (as well as spectral) time scale which we observe both theoretically and experimentally among different solvents is offered in terms of a linear response picture of the solvent as driven by the motions of the reacting molecules. This hypothesis is explored<sup>10</sup> by computing the velocity spectra of various solvents and showing that they do indeed correlate well in the frequency range of interest with the observed time scales for reaction in different solvents.

## II. MOLECULAR DYNAMICS

The computation of the molecular dynamics of solution reactions is in principle easy. We know from extensive gas phase experience that classical mechanics will usually be adequate. Given the potential energy, or the forces, linking the  $N$  atoms, and a set of initial positions  $r^N(0)$  and momenta  $p^N(0)$ , we can compute the trajectories  $r^N(t)$ , as shown in Fig. 1.

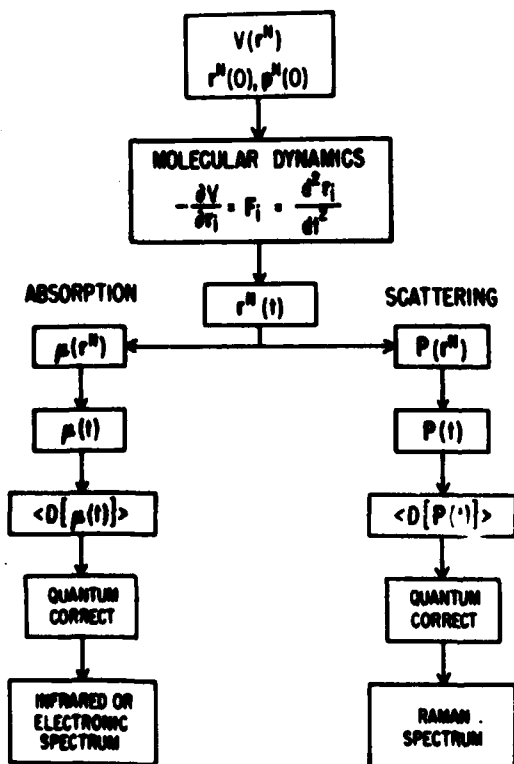


Fig. 1. Theoretical technique to compute absorption and scattering spectra from molecular dynamics. The trajectories of the atoms are calculated<sup>1,2</sup> from classical mechanics and then used to compute the time histories of the interaction with the radiation field, i.e. the dipole moment  $\mu(t)$  for absorption or the polarizability  $P(t)$  for Raman scattering. Linear response theory, ensemble averaging, and simple quantum corrections then give the infrared<sup>3,4</sup> electronic,<sup>7,8</sup> or Raman<sup>4-6</sup> spectra.

In practice there are several hurdles to be overcome. One is the synthesis of the best possible potential energy surface from the available theoretical and experimental information. We expect in the future to have to turn increasingly for guidance to *ab initio* quantum calculations, a direction in

which we have already begun to move.<sup>13</sup> A second difficulty is the sheer number of numerical operations which must be carried out to compute a statistically reliable description of the dynamics, up to  $10^{12}$  arithmetic operations for  $10^{-12}$  seconds of dynamics. This we solve by use of an array processor.<sup>1,2</sup> Other challenges include the proper handling of boundary conditions, a subject in reasonably good order for uncharged species, but not yet satisfactorily solved<sup>14</sup> for long-range Coulombic interactions, such as those involving ions.

While we do not want to minimize the effort involved in computing the molecular dynamics of solution reactions, we believe that the larger challenge now lies in sufficiently testing the dynamics against experiment so that the dynamics can either be trusted if theory and experiment agree, or improved if they do not.

### III. SPECTRA FROM MOLECULAR DYNAMICS

In this section we briefly describe some of the types of spectra which we are able to compute from solution reaction molecular dynamics, and which we wish to experimentally measure.

Following the work of Roy Gordon<sup>15</sup> we are accustomed to deducing molecular dynamics from spectra. Here we take the inverse approach and compute spectra from molecular dynamics. Specifically, from atomic trajectories we compute infrared, nonresonance Raman, and electronic spectra, as well as x-ray diffraction. Fig. 1 illustrates the general technique. From an initial set of atomic positions and velocities and the forces among the atoms we calculate from Newton's second law the atomic trajectories  $\mathbf{r}^N(t)$ . For infrared or electronic absorption spectra the molecular interaction with the radiation field is through the dipole moment  $\mu$ , and for Raman spectra through the polarizability tensor  $\Gamma$  we compute  $\mu(t)$  and  $\mathbf{P}(t)$  from  $\mu(\mathbf{r}^N)$  and  $\mathbf{P}(\mathbf{r}^N)$  as functions of nuclear positions, combined with the trajectories  $\mathbf{r}^N(t)$  as functions of time. The technique can be viewed as an expression of classical linear response theory or as an exercise in classical electromagnetic theory. We use a power spectral approach, symbolized as  $D[\ ]$ , taking advantage of fast Fourier analysis with windowing and associated corrections.<sup>3,5</sup> An average, symbolized by  $\langle \rangle$ , of the spectrum is taken over the ensemble appropriate to the experimental conditions (for example a constant temperature and density) and simple quantum corrections to the spectra are applied where needed.

#### A. Infrared

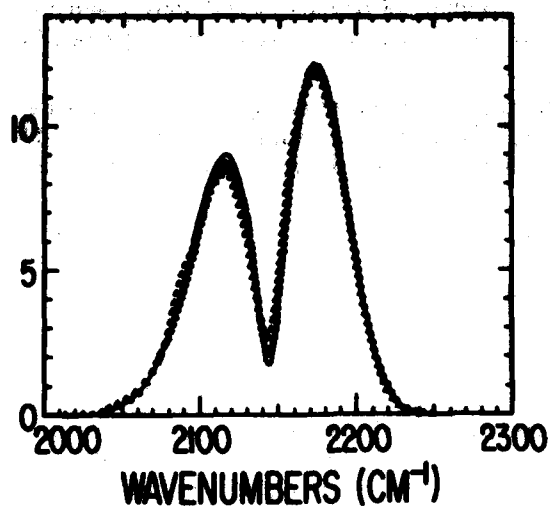
In order to compute infrared spectra, we compute the molecular dynamics, i.e. the trajectories of the atoms  $\mathbf{r}^N(t)$ , and substitute the trajectories into the dipole moment function  $\mu(\mathbf{r}^N)$  to produce the time-varying dipole moment function  $\mu(t)$ , from which, as shown in Fig. 1, the infrared spectrum is computed.

Fig. 2 shows an example of such a computed infrared spectrum, for the gas phase fundamental vibrational-rotational band contour of CO. Note that almost perfect agreement with both quantum mechanical theory and experimental measurement<sup>16</sup> is achieved by an essentially classical mechanical molecular dynamics calculation with no adjustable parameters. Elsewhere<sup>3</sup> we have also computed pure rotational absorption band contours and have extended vibrational and rotational infrared spectral calculations to the liquid phase.

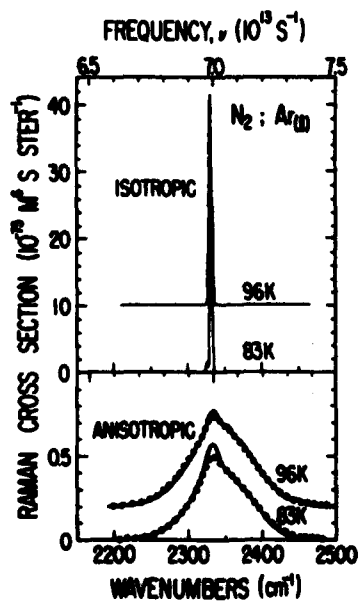
#### B. Raman

To compute nonresonance Raman spectra from molecular dynamics, we compute the time varying polarizability matrix  $\mathbf{P}(t)$  from the polarizability matrix  $\mathbf{P}(\mathbf{r}^N)$  as a function of nuclear positions and the trajectories  $\mathbf{r}^N(t)$ . Fig. 3 shows an example of an equilibrium liquid state calculation for  $\text{N}_2$  in liquid Argon at two different temperatures.<sup>5,17</sup> Again note the close agreement of molecular dynamics calculation with experiment, without the need of adjustable parameters.





**Fig. 2.** Equilibrium infrared spectrum. CO gas phase fundamental vibrational-rotational band contour. Molecular dynamics calculation as triangles,<sup>3</sup> accurate quantum calculation as straight line,<sup>3</sup> and experimental spectrum<sup>16</sup> as dotted line.



**Fig. 3.** Equilibrium Raman spectra. Fundamental isotropic and anisotropic vibrational-rotational Raman spectra for  $N_2$  in liquid Ar, at two temperatures. Molecular dynamics spectra shown as solid line,<sup>5</sup> dots from experiment.<sup>17</sup>

### C. Electronic

By using the transition dipole moment  $\mu_e(r^N)$  instead of the usual dipole moment  $\mu(r^N)$  we can again use the trajectories  $r^N(t)$  to calculate the time variation of  $\mu_e(t)$ , and from this the electronic absorption spectrum<sup>7,8</sup> in a parallel way to the infrared absorption spectrum. For sufficiently low frequency motion, as in  $I_2$ , no quantum correction is necessary. Fig. 4 shows such a computation, for  $I_2$  in liquid Xenon, of both the equilibrium  $I_2$  absorption spectrum<sup>18</sup> and of the transient absorption during the  $I_2$  photodissociation reaction sequence, which we will discuss in more detail below.

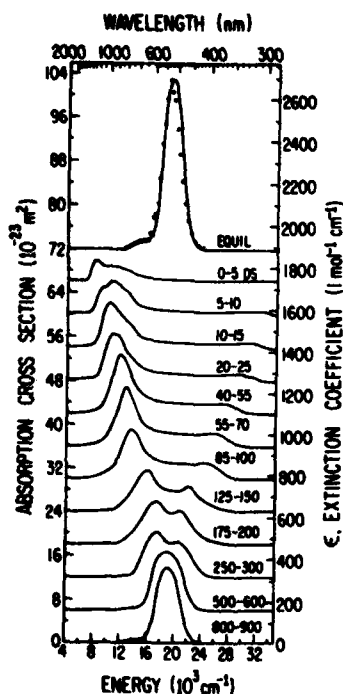


Fig. 4. Transient electronic spectrum from molecular dynamics for  $I_2$  photodissociation in liquid Xenon, made up of transitions from the ground state to the excited A, B, and B' states.<sup>7,8</sup> The computed equilibrium room temperature spectrum is shown at top with the gas phase  $I_2$  band contour as measured by Tellinghuisen<sup>18</sup> shown as dots. Below are the computed transient spectra from 0 to 900 ps for the reaction sequence beginning with photodissociative excitation to the A state, then either I atom escape or solvent caging followed by recombination to form a highly vibrationally excited  $I_2$  molecule which loses its energy to the solvent. Spectra are sequentially plotted with  $6 \times 10^{-23} \text{ m}^2$  vertical displacement.

### D. X-ray

Once we have computed the molecular dynamics, i.e. the positions of atoms as a function of time, we can then compute the x-ray diffraction as a time average over the instantaneous x-ray differential scattering cross section. The basic x-ray scattering equation is

$$\frac{d\sigma(k,t)}{d\Omega} = \left( \frac{e^2}{mc^2} \right)^2 \left( \frac{1 + \cos^2\Theta}{2} \right) \left| \int d^3r e^{ik \cdot r} \rho(r,t) \right|^2 \quad (1)$$

in which  $\frac{d\sigma(k,t)}{d\Omega}$  is the differential x-ray scattering cross section for scattering into solid angle  $d\Omega$  as a function of the photon wave (momentum) change vector  $k$  and time  $t$ ;  $k = k_f - k_i$  is the difference between the wave vector  $k_f$  of the scattered x-ray photon and the wave vector  $k_i$  of the

incident photon in which  $|k_i| = 2\pi/\lambda_i$ ,  $\lambda_i$  being the incident wavelength and the direction of  $k_i$  being the incident photon propagation direction;  $e$  is the charge on the electron,  $m$  is the electron mass;  $c$  the speed of light;  $r_e = e^2/mc^2$  is the classical radius of the electron and  $r_e^2 = 7.9398 \times 10^{-26} \text{ cm}^2$ ;  $(1+\cos^2\Theta)/2$  is the factor correcting for the use of unpolarized x-ray photons,  $\Theta$  being the scattering angle between  $k_f$  and  $k_i$ ; and  $d^3r \rho(r,t)$  is the probability for finding an electron in volume element  $d^3r$  at position  $r$  and time  $t$ .

Taking into account the molecular symmetry and the selection<sup>19</sup> of molecular alignment by the pump light, and using standard atomic structure factors,<sup>20</sup> we compute as illustrated in Fig. 5 the transient x-ray diffraction<sup>9</sup> from the  $I_2$  photodissociation reaction during the first half picosecond of the reaction sequence. Note the deviation (which is small) from cylindrical symmetry produced by the photoselection alignment. On the experimental side, in collaboration with Mourou and Williamson at Rochester, we have recently produced x-ray pulses in the hundreds of picosecond range by a light to electron to x-ray conversion process.<sup>21</sup>

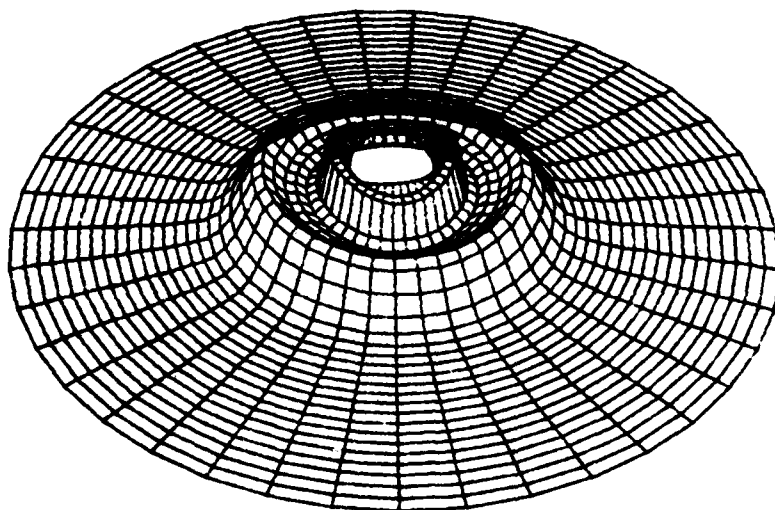


Fig. 5. X-ray diffraction for  $I_2$  dissolved in cyclohexane, calculated from molecular dynamics for the first 0.5 ps of the  $I_2$  photodissociation reaction sequence.<sup>9</sup> The diffraction is computed for Titanium  $K_\alpha$  x-rays (2.75 Å). The vertical scale is diffraction intensity, the center of the circle is scattering at  $0^\circ$  and the outer edge is scattering at  $90^\circ$ .

#### IV. TRANSIENT ELECTRONIC ABSORPTION SPECTROMETER

In order to check our computed dynamics against nature's, we have assembled a picosecond transient electronic absorption spectrometer,<sup>6,7,11,12</sup> shown in Fig. 6. A mode-locked  $Ar^+$  laser synchronously pumps two dye lasers, producing two tunable streams of picosecond pulses. Since the energy per pulse is in the nJ range, in order to achieve sufficient excitation our sample region is a small confocal volume at the focus of microscope objectives in both the pump and probe beams, which are collinear but travelling in opposite directions. The reaction solution is rapidly pumped through the confocal volume inside a small capillary. Because the cross sections for pumping and probing are both several orders of magnitude smaller than those of the strong absorbers used for most picosecond experiments, we developed a triple modulation scheme<sup>11,12</sup> using inexpensive radio amateur gear for high frequency driving and detection. This modulation system uses the discovery by Heritage<sup>22</sup> and Levine and Bethea<sup>23,24</sup> that noise in  $Ar^+$  laser systems,<sup>25,26</sup> in

particular pump-pumped, picosecond systems, falls off dramatically in the resonant region. Initial measurements with this spectrometer are described below.

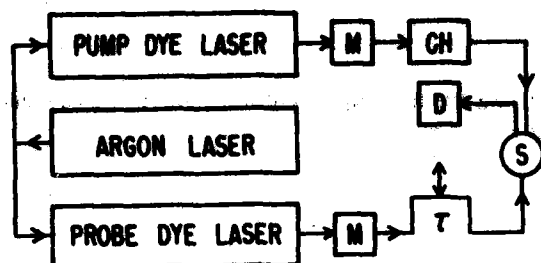


Fig. 6. Picosecond transient electronic absorption spectrometer.<sup>11,12</sup> *M* indicates a megahertz electro-optical modulator, *CH* is a mechanical chopper,  $\tau$  is the optical delay, *S* is the sample, and *D* the detector.

## V. AN EXAMPLE REACTION: $I_2$ PHOTODISSOCIATION, SOLVENT CAGING, RADICAL RECOMBINATION, AND VIBRATIONAL DECAY

Even though little is yet known, it is our belief that solution phase reaction molecular dynamics can and will be understood. The proper approach requires a combination of theoretical and experimental techniques. To this end we have already developed: i) the theoretical and computational tools<sup>2</sup> to calculate the molecular dynamics of solution reactions;<sup>6,7</sup> ii) the tools to calculate from molecular dynamics the interface to the experiment, i.e. transient spectra,<sup>3-8</sup> and transient x-ray diffraction;<sup>9</sup> and iii) the use of the experimental tool of picosecond transient electronic absorption spectroscopy,<sup>6,7</sup> as described below.

With these tools we have studied the sample case of the reaction sequence in various solvents of  $I_2$  photodissociation, solvent caging, radical recombination, and vibrational decay. The  $I_2$  reaction is a case of a diatomic involved in a simple reaction for which the electronic spectra of the reactant and that of the product (the same molecule in this special case) are sufficiently understood that transient electronic spectra can be used to decode the dynamics.

### A. Theoretical Molecular Dynamics

The first deterministic theoretical study of the molecular dynamics of solution reactions was by Bunker and Jacobson,<sup>27</sup> who computed the classical trajectories for  $I_2$  in  $CCl_4$  solvent represented by 26 spherical, structureless particles in a specular cube. Murrell, Stace and Dammel<sup>28</sup> modelled the photodissociation of  $I_2$  in dense inert gases,  $I_2$  plus 22 gas atoms in a spherical, soft-walled container.

Using the codes we have developed<sup>2</sup> and the array processor,<sup>1,2</sup> we have computed the molecular dynamics for the  $I_2$  reaction, beginning with photodissociation through the A state, in several different solvents, including ethylene glycol, cyclohexane, carbon tetrachloride, and liquid xenon.<sup>6,7,10</sup> We see dramatic differences in the molecular dynamics among the different solvents.

The conclusion of all three molecular dynamic studies, Bunker and Jacobson, Murrell, Stace, and Dammel, and our own, is that direct geminate recombination is usually a very fast process, over within a few picoseconds. An important caveat, and a weakness in these theoretical studies, is that the process whereby the  $I$  atoms dissociate on an excited state potential surface refine the ground

state surface on which they recombine is not well understood, and is therefore handled in these calculations by arbitrary assumptions which may be incorrect. If so, the real time for geminate recombination may be longer than the few picoseconds calculated. These calculations suggest, as do the non-molecular dynamic theoretical computations of Nesbitt and Hynes,<sup>29,30</sup> that the time scale of the  $I_2$  reaction sequence may be dominated by the vibrational energy decay step.

### B. Theoretical Transient Spectra

From the computed molecular dynamics, using the techniques outlined above, we calculate the transient electronic absorption spectra, shown in Figs. 4 and 7.

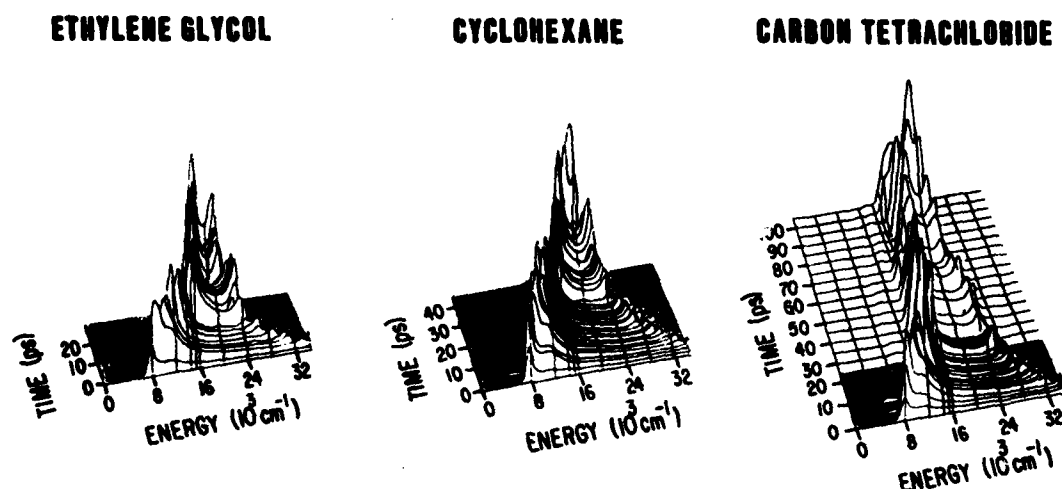


Fig. 7. Theoretical transient electronic spectra for  $I_2$  photodissociation in various solvents as computed from molecular dynamics.<sup>10</sup>

As can be seen, the differing dynamics among the solvents are reflected in differing transient spectra. The time scale of the dynamics and spectral change increases strongly in the order ethylene glycol, cyclohexane,  $CCl_4$ , i.e. in decreasing order of strength of solvent association. Thus the two absorption peaks which move in from the infrared and ultraviolet evolve back toward the original single visible peak much more slowly for the weakly associated solvents. In addition, in the 14,000 to 17,000  $cm^{-1}$  range of interest here, for higher energy probe photons the time scale of the observed transient absorption should increase, as it takes longer at higher probe energy for the infrared absorption peak to arrive and to pass by.

### C. Experimental Transient Spectra

The earliest picosecond experimental results on  $I_2$  were by the Eisenthal group,<sup>31,32</sup> who measured the transient electronic absorption spectra after excitation at 530 nm. Decay times of  $\sim 70$  ps for  $I_2$  in hexadecane and  $\sim 140$  ps in  $CCl_4$  were observed. Subsequently these studies were extended by the Eisenthal group to  $I_2$  in aromatic solvents<sup>33</sup> which are believed to form complexes with I atoms, and by Langhoff<sup>34</sup> who observed  $I_2$  photodissociation in several weakly associated liquids, finding decay times in the  $\sim 100$ – $150$  ps range. More recently, Kelley and Rentzepis<sup>35</sup> have observed  $I_2$  photodissociation in fluid and liquid Xe with a decay time of  $\sim 40$  ps, as well as in  $CCl_4$ , and similar experiments have been carried out by the Peters group.<sup>36</sup> All of the above studies used second harmonic Nd pump light at  $\sim 530$  nm, which, at least in the gas phase, results in excitation largely to the bound  $B\ 0_0^+(^3\Pi)$  state which presumably predissociates, but may absorb another photon in the meantime.<sup>37,38</sup> A delay of  $\sim 20$  ps between excitation and the minimum in the absorption curve was attributed to absorption from the B state.<sup>31,35,39</sup> Thus, the linking of these experimental transient spectra to the molecular dynamics of the  $I_2$  photodissociation and recombination reaction is made difficult by the probable presence of the additional processes of B state predissociation and absorption. We have used a different experimental approach, as described above, to pump into the dissociative A state, thus avoiding the problem of predissociation. An experimental caveat which should be remembered for all such Iodine experiments, ours included, is the well-known propensity of both I atoms and  $I_2$  molecules to form complexes, which could be involved in the observed transient spectra. Fig. 8 shows our experimental measurements of the transient electronic absorption during the  $I_2$  photodissociation reaction in different solvents at two different probe wavelengths. When the theoretical (Fig. 7) and experimental (Fig. 8) spectra are compared as a function of time, of solvent, and of probe wavelength, there is gratifyingly good general agreement.<sup>10</sup> First, as our molecular dynamics theory predicts, the time scale for the evolution of the absorption increases across the sequence ethylene glycol, cyclohexane,  $CCl_4$ . Second, the time scales are at least semi-quantitatively similar in theory and experiment. Third, the observed spectra for a particular solvent do increase in time scale as the probe photon energy is increased, again as predicted by theory. This gives hope that for the first time a major portion of the molecular dynamics of a solution reaction may indeed be understood.

### D. Interpretation of Molecular Dynamics

It would not be truly satisfying to only describe the molecular dynamics of solution reactions in terms of computer calculations, no matter how well they agree with experiment. We would like a simple physical model to unify the observed results. In this light we offer the following hypothesis which fits the presently known theoretical and experimental data.<sup>10</sup> Let us consider the solvent as a bath which is driven by the motions which the reactant molecules must go through to become products. If we think of the reaction in the frequency domain, we must drive the bath with the frequencies of the atomic motions by which the reaction occurs. To a first approximation, we can take a linear response view and just consider the natural frequency spectrum of the unperturbed solvent as the frequency response of the solvent to being forced by the reacting molecules. We take this spectrum as approximately the pure solvent velocity spectrum, i.e. the power spectrum of the velocities (or equivalently the Fourier transform of the velocity autocorrelation function) which for a harmonic system would be the normal mode density.<sup>40</sup> For the solvents of interest, these spectra are shown in Fig. 9. This simple picture is related to the more sophisticated and fully developed treatment of solution reaction molecular dynamics recently proposed by Brooks and Adelman.<sup>41-43</sup>

The frequency range of interest for the bulk of the  $I_2$  reaction time history is that of the  $I_2$  vibrational motion as it decays to the solvent, i.e. the  $100$  to  $200\text{ cm}^{-1}$  range. As Fig. 9 shows, strongly associated liquids like ethylene glycol have a high spectral density in this region because of hindered translational and rotational motion, and we would thus expect the reaction sequence to

proceed swiftly in such a solvent, as seen in both our molecular dynamics calculations reflected in Fig. 7 and our experiments as shown in Fig. 8. Cyclohexane has a lower spectral density and we would expect a slower evolution, as observed. Finally,  $\text{CCl}_4$  has the least spectral density in this frequency range, and we would expect it to be even slower, again as observed theoretically and experimentally. Thus velocity spectral density may be a unifying theme in the understanding of these reactions in solution.

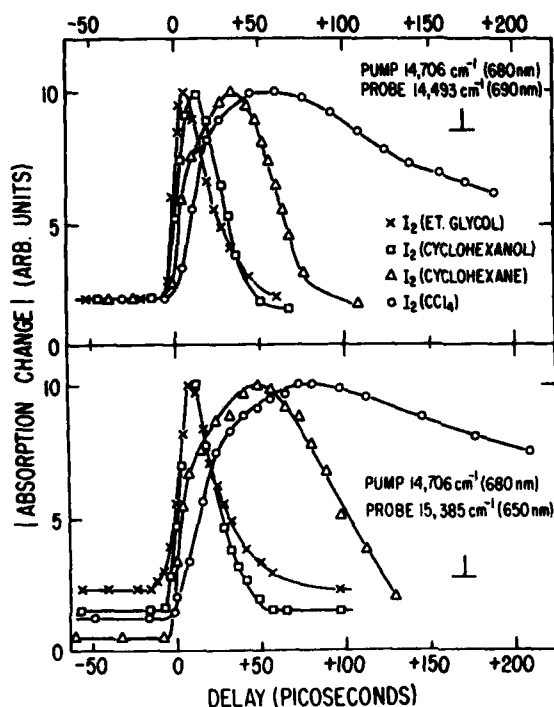


Fig. 8. Experimental transient electronic absorption spectra<sup>7,8</sup> for  $\text{I}_2$  photodissociation in various solvents at two different probe wavelengths. Note that the time scale of the observed absorption change decreases with solvent association strength and increases with probe photon energy as expected from the theoretical spectra shown in Fig. 7.

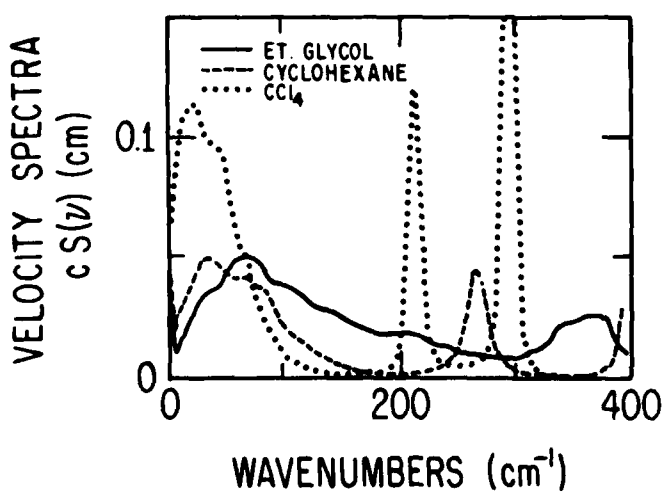


Fig. 9. Velocity spectra for various solvents as computed from molecular dynamics.<sup>10</sup>

## VI. DISCUSSION AND CONCLUSION

One of the most important unsolved questions in chemistry is how chemical reactions take place in solution in terms of the underlying motions of the atoms. We have already in place basic theoretical tools needed to solve this question for a wide variety of inorganic, organic, and biochemical reactions. We can compute the atomic motions, i.e. the molecular dynamics, for reactant-solvent systems involving hundreds to thousands of atoms for times on the femtosecond to nanosecond scale.<sup>2</sup> We can calculate from the dynamics the transient infrared,<sup>3,4</sup> Raman,<sup>4-6</sup> and electronic<sup>6-8</sup> spectra and x-ray diffraction<sup>9</sup> which reflect the underlying reaction molecular dynamics. We have now begun to test the predictions of these theoretical techniques against experimentally measured transient spectra. The agreement between theory and experiment for our first test case, the I<sub>2</sub> photodissociation reaction, is sufficiently good that we are encouraged to believe that we are at last able to discover the molecular dynamics, the microscopic process, by which a real solution takes place.

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